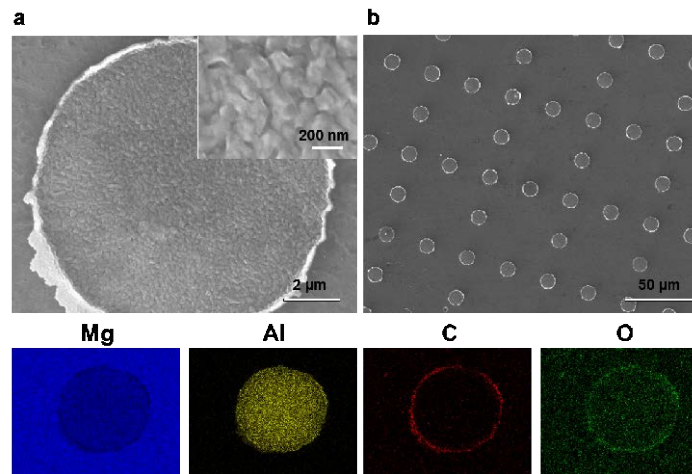


Dealloying, microstructure and the corrosion/protection of cast magnesium alloys

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Project ID# LM094

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Project start: October 1, 2013
- Project end: September 30, 2016
- 41% complete (as of March 31, 2015)

Budget

- Total Project Funding
DOE: \$ 499,961 (100%)
- Funding for FY14 (to Jan. 31, 2015) \$ 181,424
- Funding for FY15 (to Jan. 31, 2016) \$ 156, 151

Barriers

- Maintenance, repair and recycling (H)
- Performance (C)
- Predictive modeling tools (D)

Partners

Stéphane Mathieu
Université de Lorraine, Nancy France
Jonah Erlebacher
Johns Hopkins University
Roger Newman
Univ. of Toronto

Relevance and Project Objectives

Overall Project Objective: Develop the scientific foundations for understanding corrosion/protection behavior of cast Mg-Al alloys.

- To elucidate the role of alloy microstructure in terms of composition and distribution of the metallurgical phases on the micro-galvanic corrosion behavior of representative alloys such as AZ91D and AM60B.

Relevance: “The development of magnesium and its alloys to provide a clean and low cost solution to lightweighting that may also enable recycling, low cost joining, and corrosion resistance.” (from Tasks for Lightweight Materials technology)

- To develop a Kinetic Monte Carlo (KMC) simulation that incorporates pH changes and microstructural evolution that predicts corrosion behavior of Mg-Al alloys.

Relevance: Predictive Modeling Tools

- To develop Mg-Al alloy corrosion protection schemes.

Relevance: “Investigate corrosion prevention issues of magnesium with multi-material vehicle structures” (from Tasks for Lightweight Materials technology)

Relevance and Project Objectives

Specific Objectives During FY 2014 – March 31, 2015

To elucidate the role of alloy microstructure in terms of composition and distribution of the metallurgical phases on the micro-galvanic corrosion behavior of representative alloys such as AZ91D and AM60B.

- (1) The design and validation of *synthetic* Mg alloys (*via photolithography*) : This allows us to manipulate the “microstructure” in order to understand how micro-galvanic corrosion effects are connected to length scales within the alloy surface (grain size, mean separation of β -phase, etc.), local interfacial pH and diffusion boundary layer thickness (atmospheric corrosion).
- (2) The use of *ionic liquid electrolytes* (iLEs) to electrochemically quantify the anodic dissolution behaviors of the phases without the occurrence of corresponding reactions such as water reduction.
- (3) The development of a microelectrode that can be incorporated into a scanning electrochemical microscope (SECM) to measure time dependent local pH changes.
- (4) Development of a technique to measure the electrochemically surface area (ECSA) of Al on Mg alloys. Techniques such as EDS probe too deeply and measure both electrically connected and disconnected Al.

Milestones

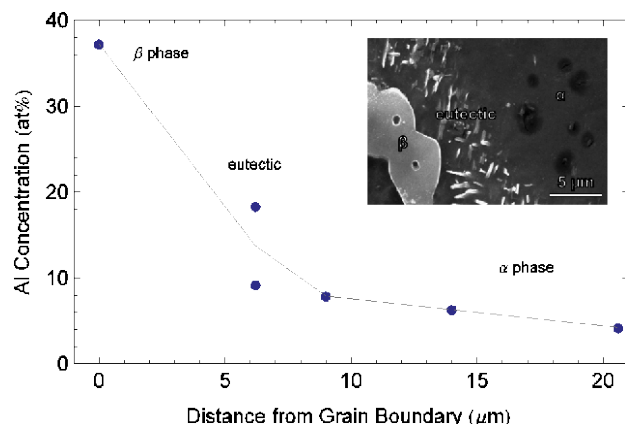
| Month/year | Milestone | Status |
|----------------|---|----------|
| September/2014 | Design/fabrication of synthetic Mg-Al alloys. | Complete |
| January/2016 | The use of ILs to clarify the anodic dissolution behavior of the dominant metallurgical phases present in Mg-Al alloys. | Ongoing |
| April/2015 | Selection of EAM potential for KMC | Complete |
| April/2015 | Validation of corrosion behavior of synthetic Mg-Al alloys. | Ongoing |
| July/2015 | Rotation Disk Electrode corrosion studies: diffusion boundary layer/microstructural length scale effects | Ongoing |

Approach

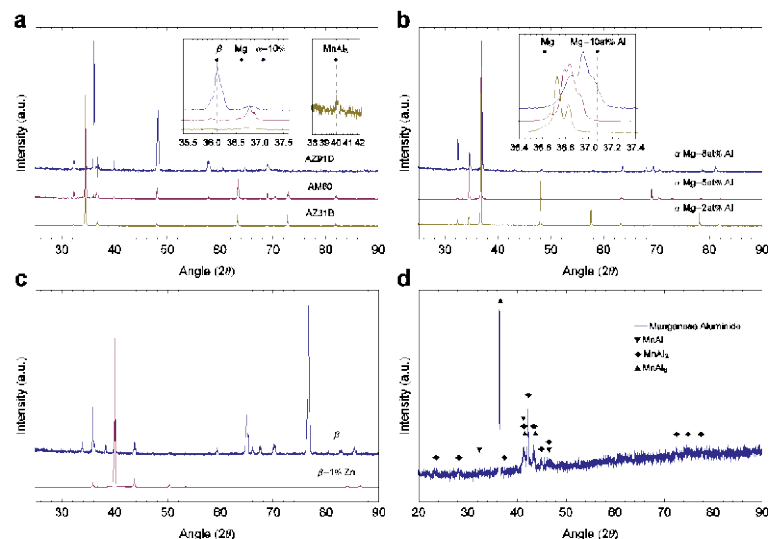
- Developed an electrochemical assay protocol using Li underpotential deposition (UPD) to determine ECSA of Al on Mg alloys. *First time such a technique has been developed.
- The electrochemical/corrosion behaviors of synthetic Mg-Al alloys are being validated. Initial electrochemical characterization results of these samples have been used to calibrate the Li UPD/Al assay protocol. The synthetic alloys allow us to “manipulate” the microstructure to separately examine how length scales can be tuned to improve corrosion behaviors.
- Compiled data on the surface morphology and composition of AZ91D, AM60 and component phases following various durations of full immersion, free corrosion in an aqueous chloride environment.
- Collected data on the electrolyte pH evolution during full immersion, free corrosion in an aqueous chloride environment of AZ91D, AM60 and component phases using a standard glass electrode.
- Synthesized an oxidized iridium microelectrode that exhibits super-Nernstian behavior that will be used in future experiments to determine how individual components in the microstructure and relative length scales between components affect pH evolution.
- Studied anodic dissolution (Mg dealloying) of Mg-Al alloy components under full-immersion in an iL and performed post mortem Al assays using EDS and Li UPD.

Technical Accomplishments

Characterized commercial alloys AZ31B, AM60B, AZ91D, α -phase Mg-Al with various Al concentrations, $\text{Mg}_{17}\text{Al}_{12}$ β -phase and manganese aluminide compounds.



Distribution of Al concentration in a balance of Mg within a representative AZ91D grain. The $\text{Mg}_{17}\text{Al}_{12}$ β phase is proximal to the grain boundary, a solid solution α phase 4-8 at% Al is located inside the grain, and between the two phases exists a eutectic region consisting of both α and β phases. The lowest Al concentration is found at the center of the grain, and it gradually increases outward toward the grain boundaries.



XRD patterns for a) commercial alloys AZ91D, AM60 and AZ31B, b) solid-solution α phase samples containing approximately 2-8 at% Al, c) $\text{Mg}_{17}\text{Al}_{12}$ β phase with and without 1% Zn and d) manganese aluminide.

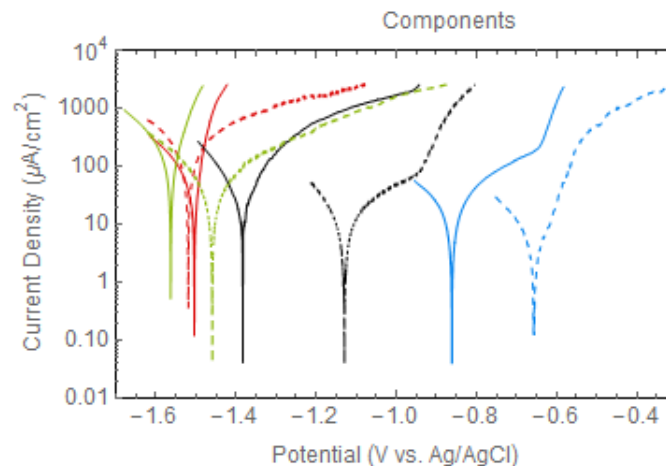
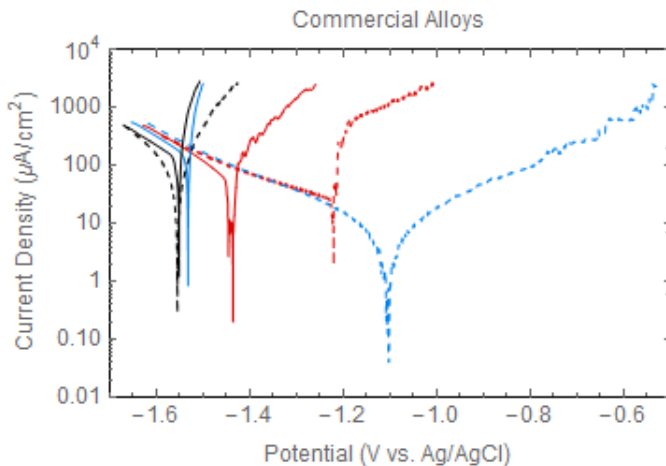
collaboration: Stéphane Mathieu
Université de Lorraine, Nancy France

Technical Accomplishments

Characterized commercial alloys AZ31B, AM60B, AZ91D, α -phase Mg-Al with various Al concentrations, $\text{Mg}_{17}\text{Al}_{12}$ β -phase, Mg and Al.

1 min —
20 Hr - - -

AZ31B
AZ31D
AM60



1 min —
20 Hr - - -

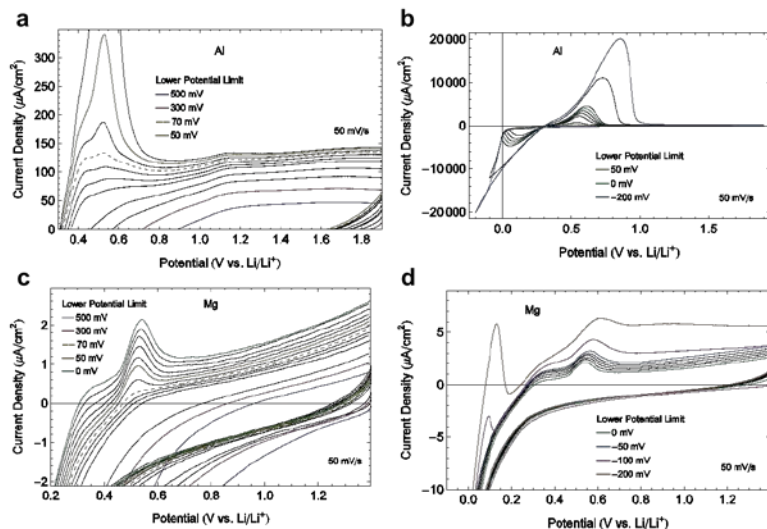
Mg 5%Al
Al
 β -Mg
Mg

| Corrosion Potential (CP) | | | |
|--------------------------|--------------------------|---------------------------|-----------------------------------|
| Sample | CP, 0 hr (V vs. Ag/AgCl) | CP, 20 hr (V vs. Ag/AgCl) | ΔCP (V vs. Ag/AgCl) |
| AZ31B | -1.44 | -1.22 | 0.215 |
| AZ91D | -1.53 | -1.11 | 0.425 |
| AM60 | -1.55 | -1.56 | -0.004 |
| Mg5Al | -1.5 | -1.52 | -0.015 |
| Al | -0.86 | -0.66 | 0.205 |
| β -Mg | -1.38 | -1.13 | 0.254 |
| Mg | -1.56 | -1.46 | 0.104 |

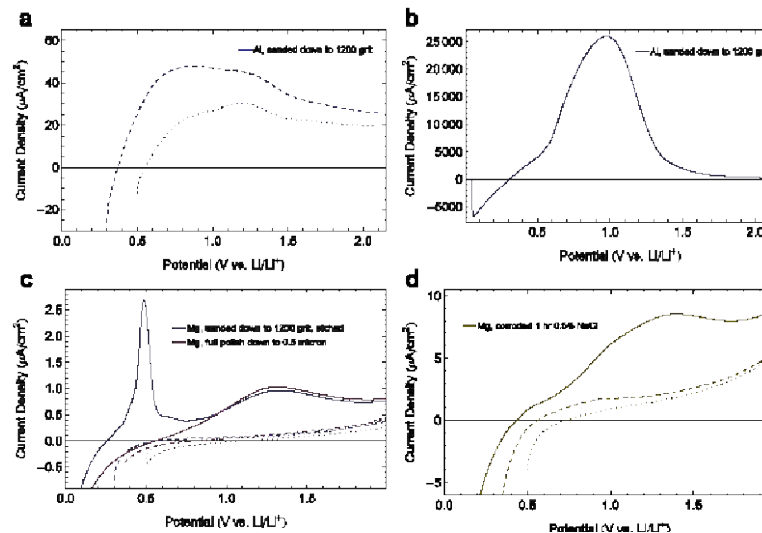
Shift in Corrosion Potential over 20 Hr. immersion in 3.5% NaCl Electrolyte

Technical Accomplishments

Li UPD for the determination of the ECSA of Aluminum



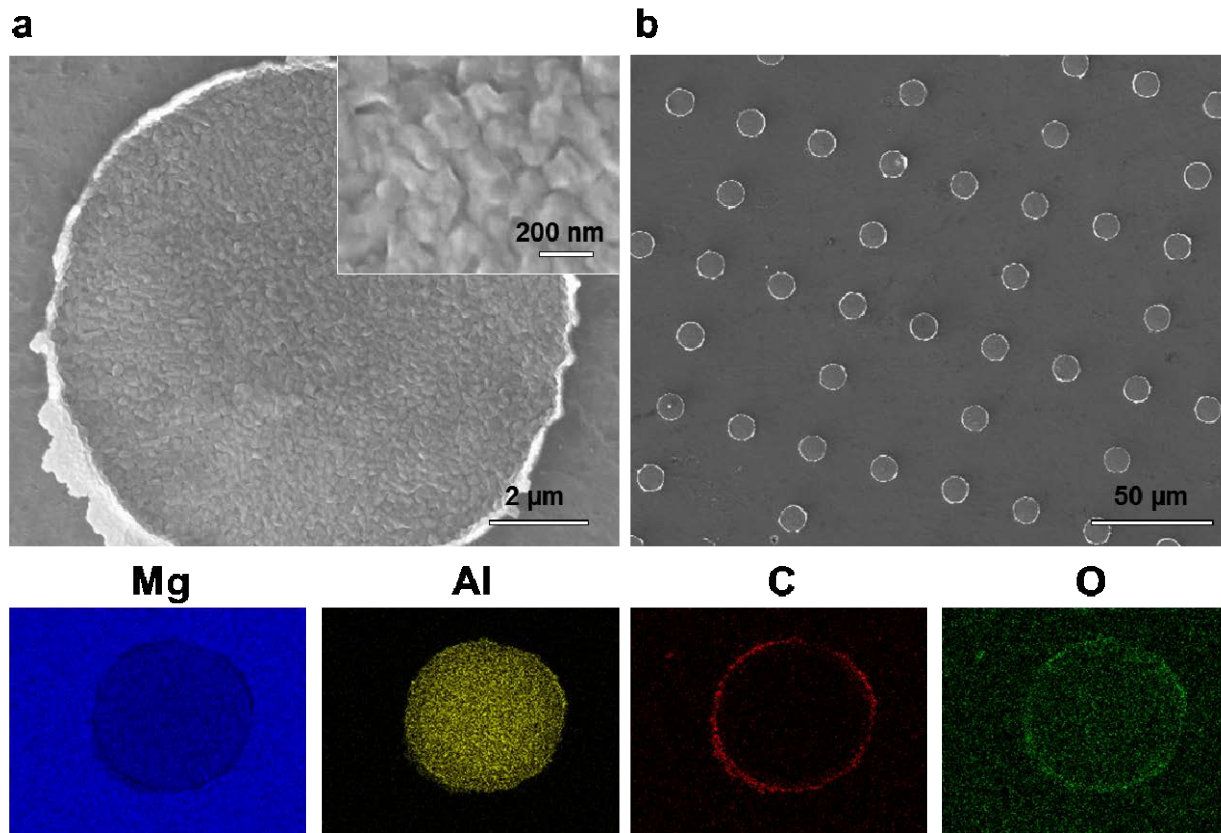
Cyclic voltammetry performed at 50 mV/s in 1.0 M LiClO₄ in propylene carbonate at increasingly lower potential limits for a, b) Al sheet, 99.999%, and c, d) Mg, 99.95% sanded down in a UHP Ar atmosphere to minimize native oxides effects. Significant traces are labeled by the CV lower potential limit vs. Li/Li⁺.



Anodic stripping curves at 5 mV/s in 1.0 M LiClO₄ in propylene carbonate following 600 second chronoamperometry at the lower potential limit: (dotted) 500 mV, (dashed) 300 mV and (solid) 50 mV vs. Li/Li⁺ for a, b) Al sheet, 99.999%, and Mg, 99.95% for various preparations: c) sanded and d) corroded under full immersion in 0.5% aqueous NaCl for 1 hr.

Technical Accomplishments

Synthetic Mg-5at% Al alloy surface produced by photolithography



SEM surface morphology of 5%, 100 nm thick Al coverage on 99.95% Mg substrates that underwent sputtering during photolithography at a) higher magnification showing the deposit texture and b) lower magnification showing the overall pattern. EDS areal mapping was performed on the island in a) to show the elemental mapping of Mg, Al, C and O.

Technical Accomplishments

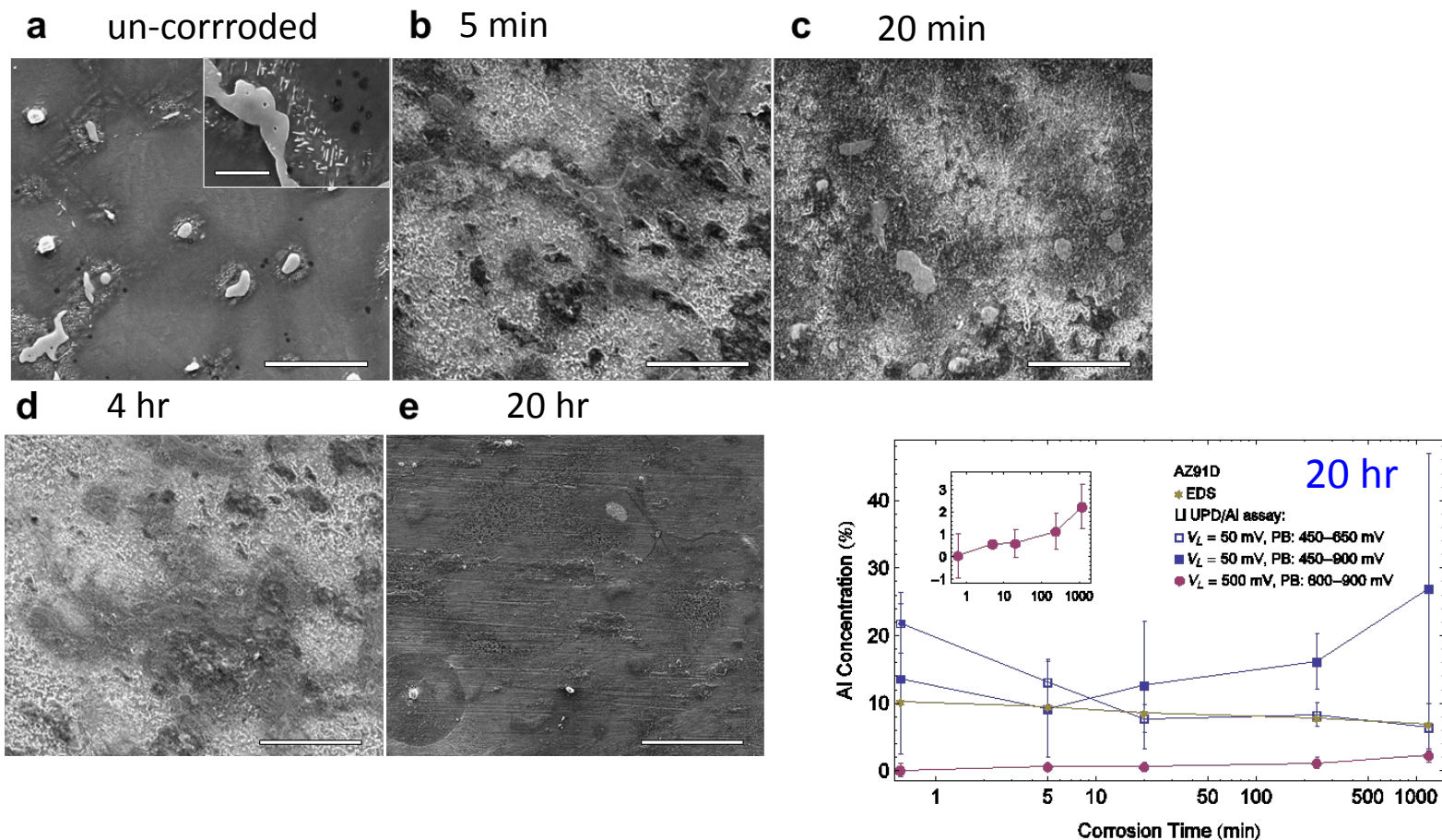
Validation: Li UPD ECSA determination of the synthetic Mg-5 at% Al alloy (Also validated for real Mg-5 at% Al alloy)

Li UPD/Al assay for synthetic alloy containing 5 at% Al.

| Stripping curve following 600 s at lower potential mV (vs. Li ⁺ /Li) | Peak location mV (vs. Li ⁺ /Li) | | Stripping charge density (μC/cm ²) | | Al (%) (from stripping charge at peak potential) |
|---|--|-------------|--|----------------------------|--|
| | 100% coverage | 5% coverage | 100% coverage | 5% coverage | |
| 500 | 910 | 1050 | 320 | 6.4-25 | 5 ± 4 |
| 300 | 489/755 | 450/910 | 650 | 30-65 | 7 ± 4 |
| 50 | 287 567 | 280 493 | 230 2.7x10 ⁴ | 8.1 3.0x10 ² | 3.5 1.1 |

Technical Accomplishments

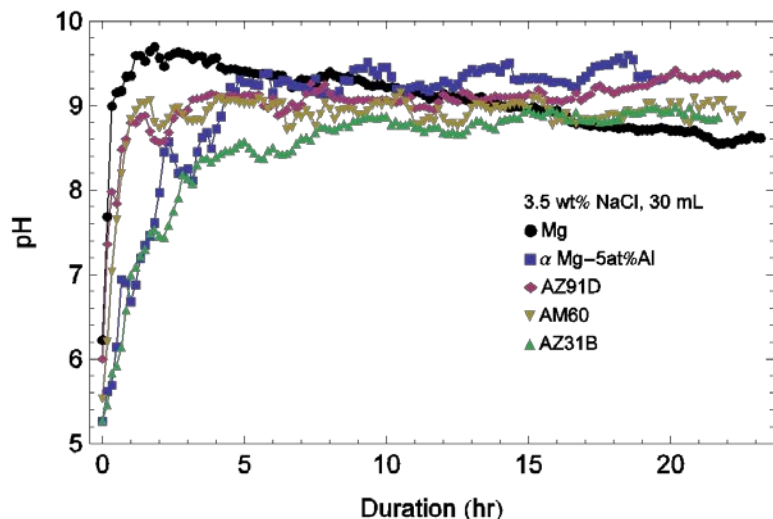
Surface morphology and composition/Al redistribution for AZ91D following various durations of full immersion, free corrosion in an aqueous chloride environment.



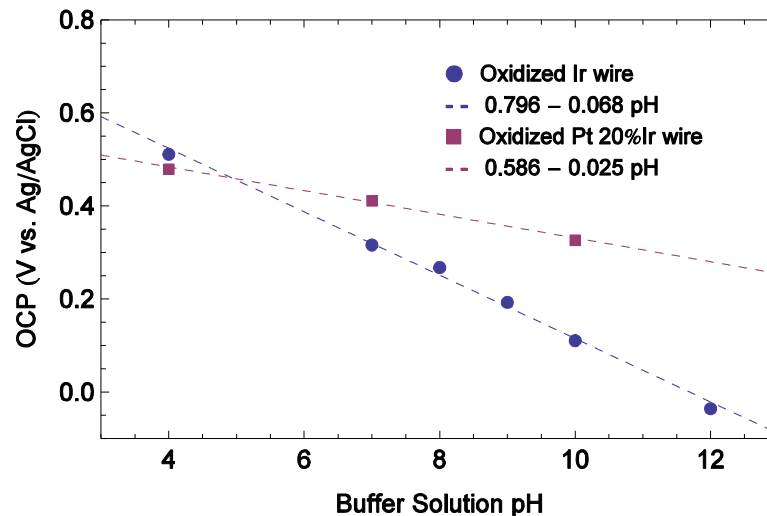
SEM images for indicated times and Li UPD and EDS /Al assay results for 20 hr. free corrosion of AZ91D in 3.5% aqueous NaCl. Scale bars are 50 μ m for the main images and 10 μ m for the inset.

Technical Accomplishments

Developed oxidized iridium and Pt-Ir microelectrodes that that will be used in future experiments using scanning electrochemical microscopy to access how microstructural length scales in real and synthetic alloys affect pH evolution.



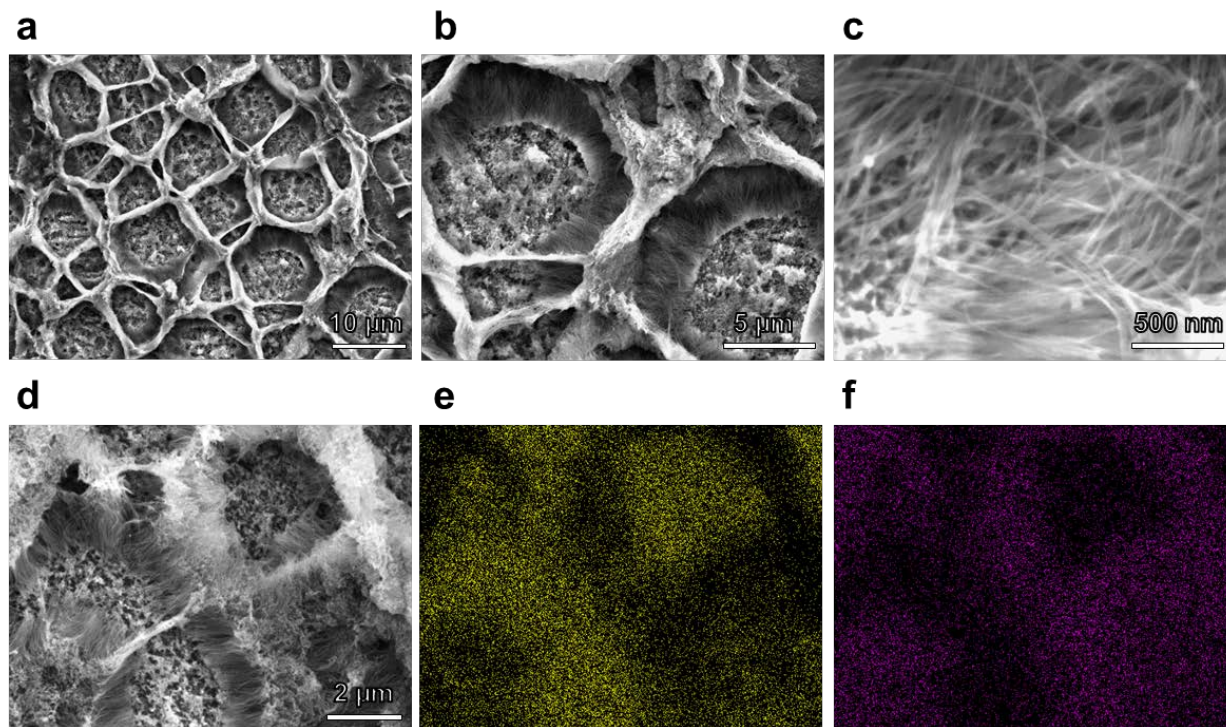
Evolution of electrolyte pH of commercial alloys and common components under full immersion, free corrosion in 3.5% aqueous NaCl using a standard glass electrode.



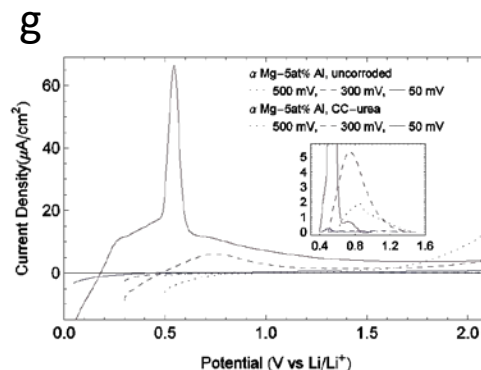
Calibration curve relating the open circuit potentials of the oxidized microelectrode made from Ir and Pt-20% Ir wires with respect to the solution pH

Technical Accomplishments

Anodic dissolution of α Mg-5 at% Al in an iL; post mortem Al assays using EDS and Li UPD.



Step-flow dissolution of Mg results in the accumulation of solid solution Al and the formation of Al nanowires



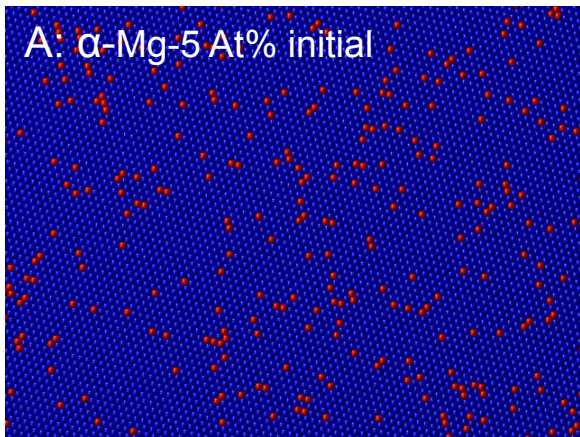
Surface morphology using SEM of α Mg-5 at% Al, (Grain size \sim 100 μ m) following potentiostatic corrosion at -100 mV vs. Al/Al³⁺ for 60 min in a deep eutectic 1:2 molar ratio of choline chloride:urea at 150 ° C shown at increasing magnification (a-c) as well as EDS areal mapping of the base, nanowire and ridge morphology shown in d) for e) Mg and f) Al abundance. g) Li UPD assay: equivalent \sim 80% Al surface coverage

Technical Accomplishments

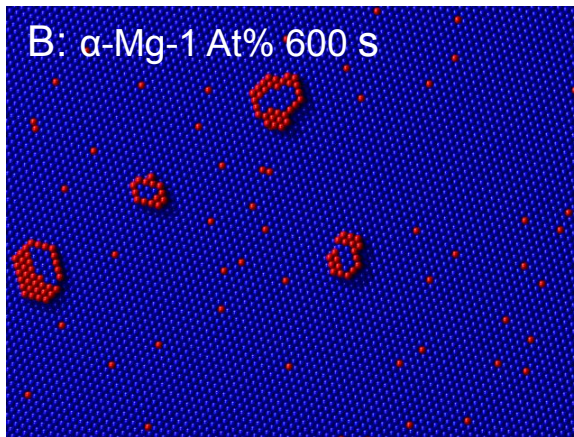
Preliminary KMC simulations of α -phase corrosion

Collaboration: Jonah Erlebacher
Johns Hopkins University

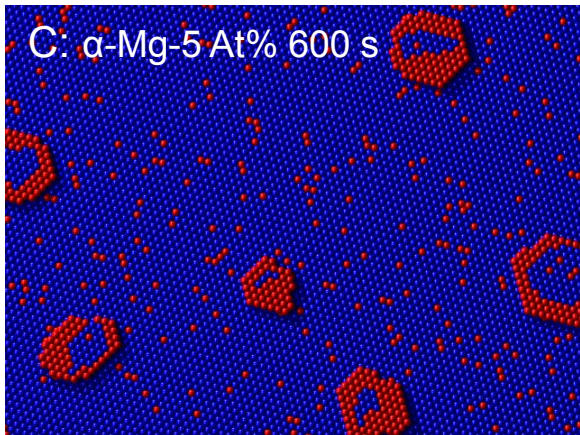
A: α -Mg-5 At% initial



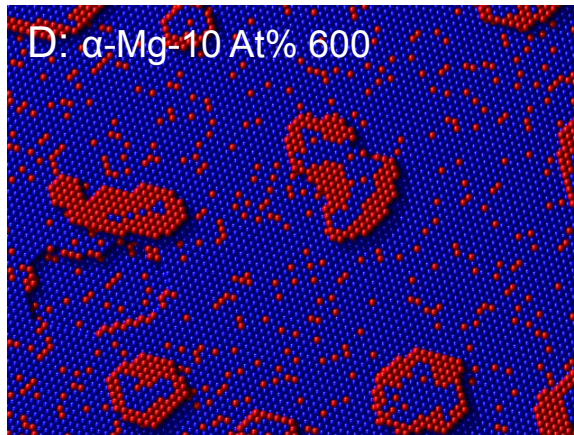
B: α -Mg-1 At% 600 s



C: α -Mg-5 At% 600 s



D: α -Mg-10 At% 600



KMC simulation (near-neighbor regular solution model) results showing the redistribution of solid solution Al after 600 seconds of free corrosion of α -Mg. Al atoms are in red and the Mg atoms are in blue. **(A)** Mg-5%Al solid solution *alloy prior to corrosion*. **(B)** Mg-1%Al **(C)** Mg-5%Al **(D)** Mg-10%Al. The initial composition of the α -Mg sets the surface density and size of the redistributed Al clusters evolving on the surface of the alloy. These Al clusters are constantly forming and being under-cut by the corrosion process and serve as active cathodes for water reduction.

Response to Reviewers Comments

This project started in October 2013 and was not reviewed last year.

Collaborations

Stéphane Mathieu: Université de Lorraine, Nancy France (outside VT program)
Academic collaboration

We are collaborating on the behavior of 2nd phase (α -phase, $\text{Mg}_{17}\text{Al}_{12}$ β -phase, manganese aluminide compounds) electrochemical behavior. Stéphane has supplied us with these stand-alone 2nd-phase species.

Jonah Erlebacher: Johns Hopkins University (outside VT program)
Academic collaboration

We are collaborating on the Kinetic Monte Carlo simulations of Mg-Al alloy corrosion. He and the PI are working through various schemes for including pH changes and passivation into *MESOSIM* which is the code developed by Jonah for alloy corrosion.

Roger Newman: Univ. of Toronto (outside VT program)
Academic collaboration

Roger and the PI regularly discuss various aspects of Mg-Al alloy corrosion. Interchange of scientific ideas.

Remaining Challenges and Barriers

Development of a Kinetic Monte Carlo (KMC) simulation that incorporates pH changes and microstructural evolution that predicts corrosion behavior of Mg-Al alloys.

- Efficient algorithm for incorporating pH changes for atmospheric and/or full immersion corrosion.
- Data for the rate constants of chemical dissolution of oxides-to be determined using inductively coupled plasma mass spectroscopy (ICP-MS)

Development of Mg-Al alloy corrosion protection schemes.

- KMC identification of alloying element(s) to achieve stainless-like behavior.

Future Work

- Continue to fabricate and validate synthetic Mg-Al alloy behavior with real alloys using electrochemical characterization: **Q7 milestone**
- Expand the study of Mg-Al corrosion in non-aqueous ionic liquids to determine the effect of parameters such as duration and electrochemical potential on morphology and aluminum redistribution and enrichment: **Q9 milestone**
- Perform atmospheric corrosion studies on both real and synthetic alloys. **Q8 milestone**
- Perform KMC simulations incorporating embedded atom (EAM) potentials to ascertain the anodic dissolution behavior of Mg-Al alloys: **Q9 milestone**
- Develop and test hydrophobic coatings using aprotic hydrophobic ionic liquids: **Q12 milestone**
- Develop and test stainless-like Mg alloys identified using KMC simulations: **Q12 milestone**

Summary

Relevance

- Clean and low cost solution to lightweighting.
- Predictive modeling tools.
- Corrosion prevention of Mg alloys.

Approach

- Assay for Al ECSA
- Examining the effect of microstructural length scales and diffusion boundary layer thickness on micro-galvanic corrosion in aqueous chloride: Free corrosion studies of real and synthetic Mg-Al alloys. Assay for Al ECSA
- Anodic dissolution of real and synthetic Mg-Al alloys in an iL.; Assay for ECSA
- KMC simulations of alloy corrosion.
- Corrosion protection

Technical Accomplishments

- Al ECSA assay; Li UPD
- Development of pH oxidized Ir and PtIr microelectrodes; SECM
- anodic dissolution of Mg-Al alloys under full-immersion, potentiostatic corrosion in an iL and performed post mortem EDS and Li UPD/Al assays.
- Time dependent pH changes during free corrosion in an aqueous chloride electrolyte.
- Selection of EAM potential for KMC simulations.

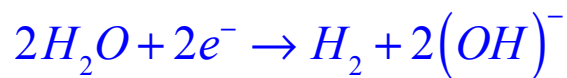
Future Research

- Atmospheric corrosion
- KMC simulations
- Examine hydrophobic coatings for corrosion protection.
- Develop and test stainless-like Mg alloys identified using KMC simulations

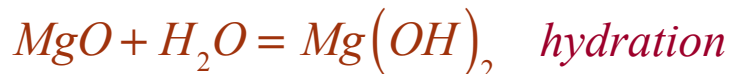
Technical back-up slides

General scenario for the corrosion of Mg-Al alloys

- In near-neutral electrolytes containing chloride, second phase particles such as the $\text{Mg}_{17}\text{Al}_{12}$ β -phase serve as cathodes for water reduction resulting in spatially localized increases in pH.



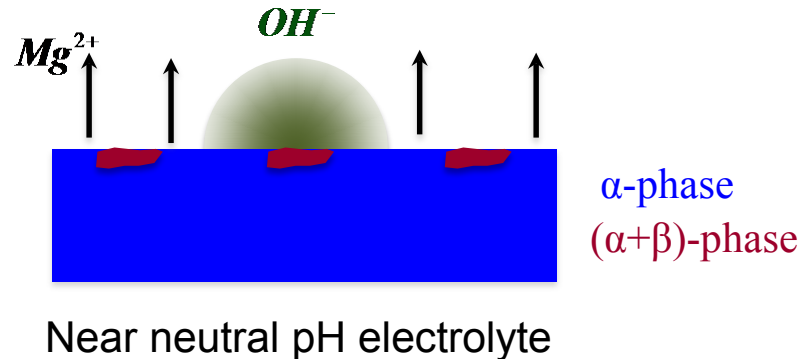
- The corresponding dissolution reaction involves the dealloying of Mg from α -matrix grains necessarily resulting in enrichment and redistribution of solid solution Al.



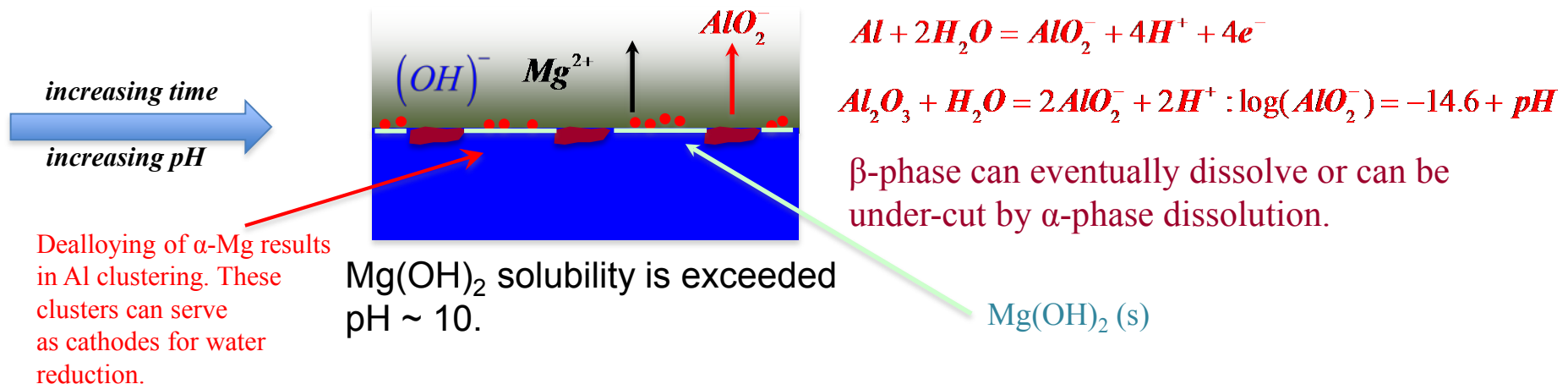
The solubility of $\text{Mg}(\text{OH})_2$ in water at RT is $\sim 10^{-3} \text{ M}$ so the system will tend to “self-buffer” at pH ~ 10

General scenario for the corrosion of Mg-Al alloys

Primary corrosion process of alloys such as AZ91D



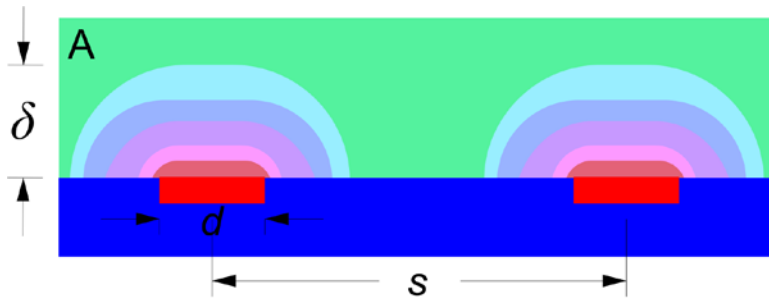
Secondary corrosion processes



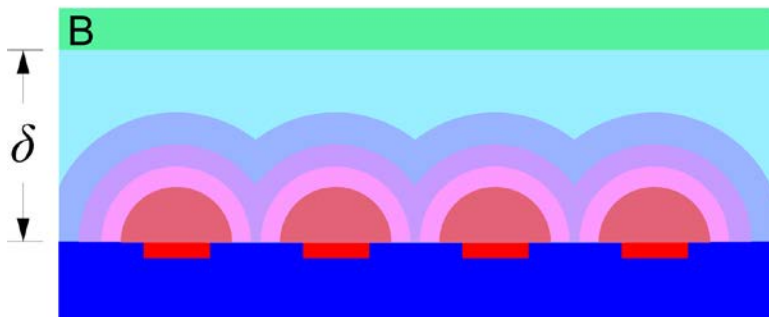
General scenario for the corrosion of Mg-Al alloys

Important Length Scales in the Corrosion Process

Length scales and local pH change during Mg-Al alloy corrosion. **(A)** and **(B)**: Schematic illustration of the growth and overlap of zones of elevated pH as a function of the cathode particle size, d and spacing s . δ is the thickness of the diffusion boundary layer. The shaded colors correspond to the shape and extent of a pH 9.5-10 zone as time evolves.



(A) $d \sim \delta$, $s \gg \delta$. Particle separation is significantly larger than the diffusion boundary layer thickness and zones of increasing pH are cut off by convection changing the three-dimensional hydroxide diffusive flux to a 2-dimension field. Hence, only the α -Mg matrix immediately adjacent to the particles may be exposed to a high enough pH for α -phase passivation to occur.

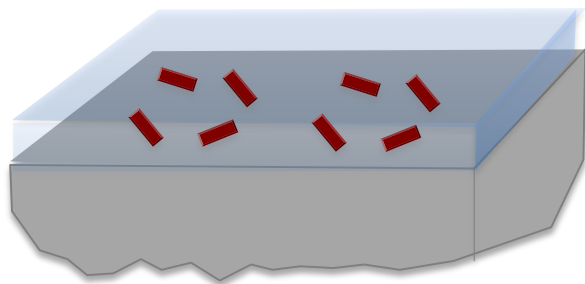


(B) $d \ll \delta$, $s \ll \delta$. Particle size and separation are considerably smaller than the diffusion boundary layer thickness, the system behaves as a micro-electrode array, causing the entire surface to passivate.

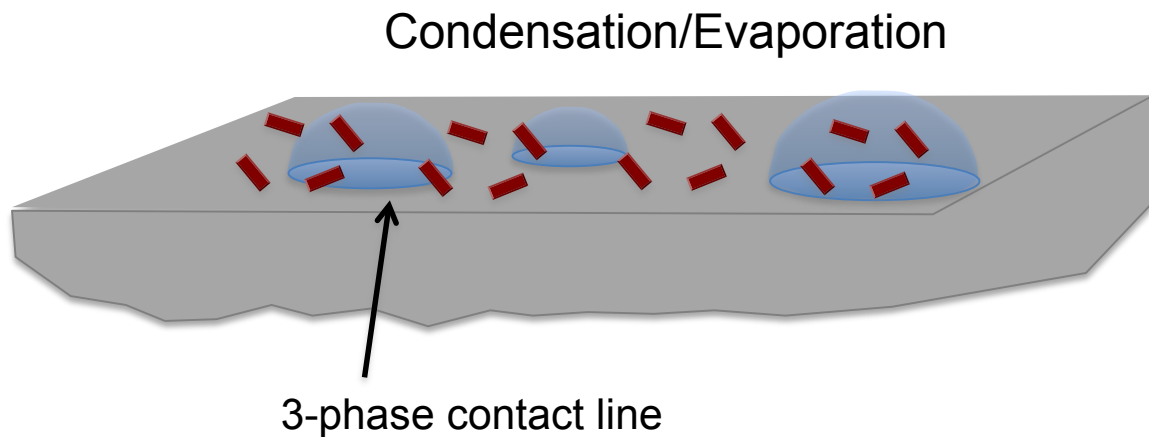
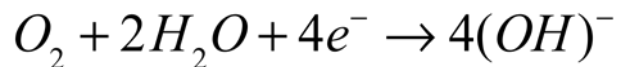
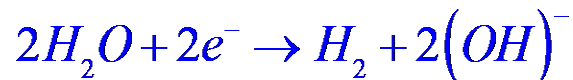
General scenario for the corrosion of Mg-Al alloys

Important Length Scales in the Corrosion Process

Atmospheric corrosion: droplet size, condensed electrolyte layer thickness sets the electrolyte length scale. Additionally oxygen reduction at the contact line may contribute to overall cathodic processes.



~10 μm thick electrolyte layer



Oxygen reduction may significantly contribute to reduction processes during atmospheric corrosion.